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(71) Applicant
Sandoz Ltd

(Incorporated in Switzerland)

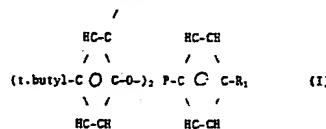
35 Lichtstrasse, CH-4002 Basle, Switzerland

(72) Inventors
Jean-Paul Kehrl
Rainer Wolf

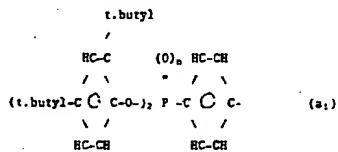
(74) Agent and/or Address for Service
B A Yorke & Co
Coomb House, 7 St John's Rd, Isleworth, Middlesex,
TW7 6NH, United Kingdom

(54) Stabilisers for polymers

(57) A processing stabiliser for polymers comprises
a) 30-80% by weight of a compound or formula I



in which R_1 is hydrogen, methyl, unsubstituted phenyl or a group of formula a₁)



in which n is 0 or 1;

b) 20-70% by weight of a phosphite compound; and optionally c) and antioxidant.

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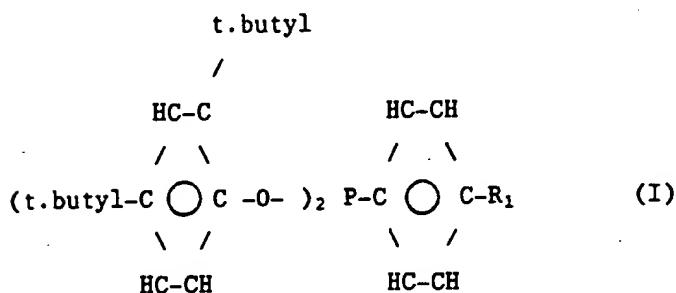
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IMPROVEMENTS IN OR RELATING TO ORGANIC COMPOUNDS

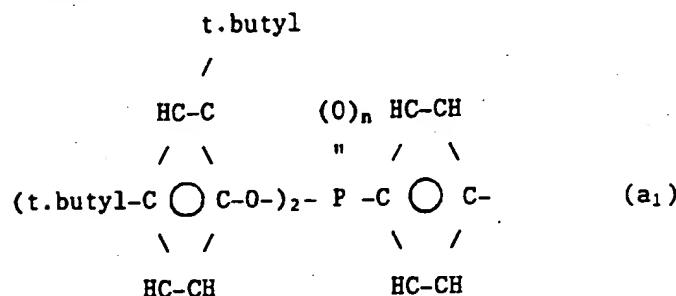
The invention relates to a mixture of a phosphonite and a phosphite stabiliser for polymeric substrates.

According to the invention, there is provided a composition for use as a processing stabiliser (herein defined as a stabilising composition), comprising

a) 30-80% by weight of a compound of formula I



in which R_1 is hydrogen, methyl, unsubstituted phenyl or a group of formula a_1)



in which n is 0 or 1 or mixtures thereof; (herein defined to as component a); and

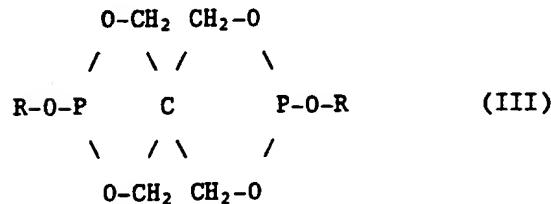
b) 20-70% by weight of an organic phosphite compound (herein defined as component b).

Usually component a) will be a mixture of a mono- and di-phosphonite.

Compounds of formula I and component b) are antioxidants.

Preferably a composition according to the invention contains one or more additional antioxidants (for example sterically hindered phenolic antioxidants, aminoaryl antioxidants or sulphur containing antioxidants).

Preferred phosphites are those of formula II or III



in which each R, independently, is a linear or branched C₁₋₂₂ alkyl or phenyl, unsubstituted or substituted by 1 to 3 linear or branched C₁₋₁₂alkyl groups (preferably methyl or t.butyl).

More preferred phosphites of a stabilising composition according to the invention are selected from tris-(2,4-di t.butylphenyl) phosphite, tris (nonylphenyl) phosphite, trilauryl phosphite, bis

(2,6-di-t.butyl-4- methylphenyl) pentaerythrityl-diphosphite, bis (2,4-di-t.butyl phenyl) pentaerythrityl-diphosphite and distearyl-pentaerythrityl diphosphite.

Preferred phenolic antioxidants are selected from octadecyl-3-(3',5'-ditert.butyl-4'-hydroxyphenyl)-propionate, pentaerythrityl-tetrakis-3-(3',5'-ditert.butyl-4'-hydroxyphenyl)-propionate, 1,3,5-tris-(3',5'-di-t-butyl-4'-hydroxy-phenyl)-isocyanurate, 1,1,3, tris-(5'-tert.butyl-4'-hydroxy-2'-methylphenyl)-butane, 1,3,5-tris-(3',5'-ditert.butyl-4'-hydroxybenzyl)-mesitylene and ethylene glycol-bis-(3,3-bis-(3'-tert.butyl-4'-hydroxyphenyl)-butyrate).

Preferred aminoaryl antioxidants are selected from N,N'-dinaphthyl-p- phenylene diamine and N,N'-hexamethylene bis-3-(3,5-ditert.butyl-4- hydroxyphenyl)-propionamide.

Preferred sulphur containing antioxidants are selected from di-tridecyl-3,3- thiodipropionate, di-lauryl-3,3'-thiodipropionate, distearyl-3,3' -thiodipropionate, methane tetrakis- (methylene -3-hexyl thiopropionate) and dioctadecyl-disulphide .

A further preferred additive to a stabilising composition according to the invention is alpha tocopherol (Vitamin E).

Preferably, in a composition according to the invention, the amount of component a) present is from 70 to 40% by weight and the amount of component b) present is from 30 to 60%, by weight of the composition. More preferably in a composition according to the invention, the amount of component a) present is 40-60% by weight and the amount of component b is 60-40% by weight of the composition.

Preferably, if an antioxidant (or Vitamin E) is present, it is present in an amount of 50 to 200%, by weight of components a) and b) of a composition according to the invention.

Further, according to the invention, there is provided a polymeric composition comprising a polymeric material and a stabilising amount of a stabilising composition according to the invention.

Preferably the total amount of components a) and b) present in such a polymeric composition is from 0.01 to 1 %; more preferably 0.05 to 0.3 % by weight based on the polymeric material.

It has been found that a combination of a) and b) in a stabilising composition according to the invention produces a synergistic effect on the stability of a polymeric composition to which it is applied. Properties such as yellowing (as measured using the yellowness index) and the melt flow index (MFI) of such polymeric compositions are significantly improved over those in which only component a) or b) is present.

Preferred polymeric materials to be stabilised are polyolefins such as polypropylene, polyethylene (e.g. high density polyethylene, low density polyethylene, linear low density polyethylene or medium density polyethylene), polyisobutylene, poly-4-methylpentene and copolymers thereof (such as EVA-ethylene vinyl acetate).

Further polymeric materials that can be stabilised by a stabilising composition according to the invention include polystyrene and copolymers and blends thereof, ABS, polyvinyl acetate, polyvinylalcohol, polyacetate (POM), polyacrylate and polymethacrylate, polyacrylonitrile, polyacrylamide, PVC, polyvinylidene chloride, polyamide, polyester (for example polybutylene terephthalate and polyethylene terephthalate), polyether (e.g. polyphenylene oxide - PPO), polythioether and thioplast, polycarbonate, polyurethane, cellulose derivatives, maleinate resins, melamine resins, phenolic resins, aniline resins, furane resins, carbamide resins, epoxide resins and silicon resins.

Further additives that can be added to a stabilising or a

polymeric composition according to the invention include flame retardants, antistatic agents, U.V. stabilisers such as hindered light amine stabilisers and U.V. absorbers (e.g. 2-(2'-hydroxyphenyl)-benztriazoles, 2-hydroxybenzophenones, 1,3-bis-(2'-hydroxybenzoyl)-benzene salicylates, cinnamates and oxalic acid diamides;), U.V. quenchers such as benzoates and substituted benzoates, sterically hindered amines (for example N-unsubstituted, N-alkyl or N-acyl substituted 2,2,6,6-tetra-methylpiperidine compounds), softeners, nucleating agents, metal deactivators, biocides, impact modifiers, fillers, pigments and fungicides.

Stabilising compositions according to the invention may be added to the polymeric material before, during or after the polymerization step and may be added in solid or molten form, in solution preferably as a liquid concentrate containing from 10 to 80 % by weight of the composition and 90 to 20 % by weight of solvent or as a solid masterbatch composition containing 10 to 80 % (more preferably 40 to 70 %) by weight of the composition and 90 to 20 % (more preferably 60 to 30 %) by weight of a solid polymeric material which is identical with or compatible with the material to be stabilized.

The compositions according to the invention may be incorporated by known methods into the polymeric material to be stabilized. Of particular importance is blending of the compounds with thermoplastic polymers in the melt, for example in a melt blender or during the formation of shaped articles, including foils, tubes, fibres and foams by extrusion, injection moulding, blow moulding, spinning or wire coating. The compositions according to the invention are particularly useful for polypropylene fibres or foils.

Further, in this specification, where a range is given, the figures defining the range are included therein. Any group capable of being linear or branched is linear or branched unless indicated to the contrary.

For the avoidance of doubt, in this specification t-butyl means

tertiary butyl.

The invention will now be illustrated by the following Examples in which all parts and percentages are by weight and all temperatures are in °C unless indicated to the contrary.

EXAMPLE 1

A solution is made up as follows:

1 g. of calcium stearate,
1 g. of pentaerythrityl-tetrakis-3-(3',5'-di-t.butyl-4'-hydroxy-phenyl)-propionate,
0.4 g. of tetrakis-(2,4-di-t.butyl-phenyl)-4,4'-biphenylene-diphosphonite, and
0.4 g. of tris (2,4-di-t.butyl-phenyl)-phosphite, and
0.2 g. of bis(2,4 di-t.butylphenyl) diphenyl phosphonite
(=0,0'-bis(2,4-ditertiarybutyl)biphenylphosphonite)
dissolved in 25 mls of acetone.

This solution is added to 1000 g of polypropylene powder and is mixed for 5 minutes at 400 revs per minute. The powder is dried for 30 minutes at 50°C in an oven and subsequently compounded in a Göttfert extrusiometer having a 20 mm screw (compression 1:3, diameter to length [d:l] = 1:20) at 270°C. Multiple extrusions are carried out under the same conditions. The Melt Flow Index (MFI) is determined at 230°C/2.16kp and is used to characterise the stabilisation efficiency.

EXAMPLES 2 to 4

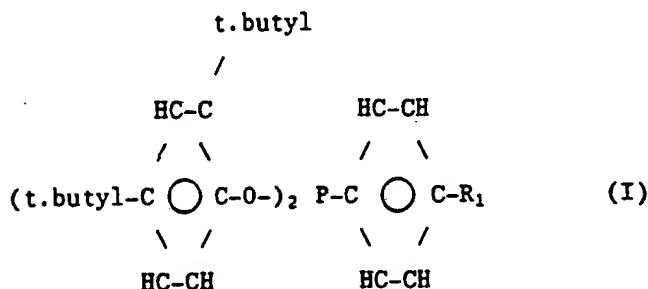
Example 1 is repeated using, instead of 0.4 g. of the tris (2,4-di-t.butyl- phenyl) phosphite, 0.2 g of the tris (2,4-di-t.butyl- phenyl) phosphite and 0.2 g. of one of the following:

Example 2 : tris-(nonylphenyl)phosphite;
Example 3 : a 40:60 mixture of alpha tocopherol (Vitamin E) and tris-(nonylphenyl)-phosphite; and
Example 4 : a 20:40:40 mixture of alpha tocopherol (Vitamin E), di-tridecyl-3,3'-thiodipropionate and tri-lauryl-phosphite.

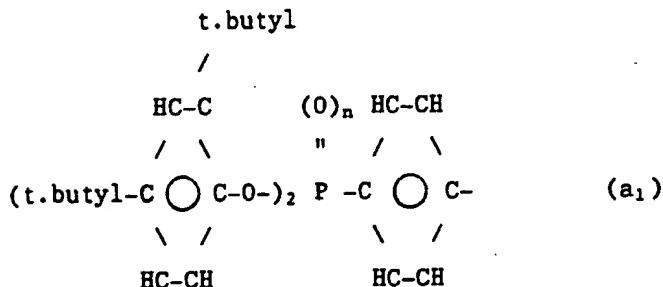
CLAIMS: -

1. A composition for use as a processing stabiliser (herein defined as a stabilising composition), comprising

a) 30-80% by weight of a compound of formula I



in which R_1 is hydrogen, methyl, unsubstituted phenyl or a group of formula a_1)

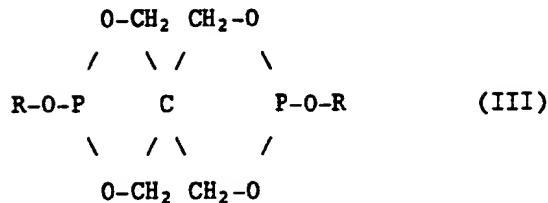
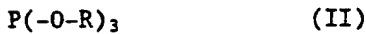


in which n is 0 or 1; (herein defined to as component a); and

b) 20-70% by weight of a phosphite compound (herein defined as component b).

2. A composition according to Claim 1 in which component b is

selected from one or more compounds of formula II or III



in which each R, independently, is a linear or branched C₁₋₂₂ alkyl or phenyl, unsubstituted or substituted by 1 to 3 linear or branched C₁₋₁₂ alkyl groups.

3. A composition according to Claim 2 in which component b) is selected from tris-(2,4-di-t.butylphenyl) phosphite, tris (nonylphenyl) phosphite, trilauryl phosphite, bis (2,6-di-t.butyl-4-methylphenyl) pentaerythrityl-diphosphite, bis (2,4-di-t.butyl phenyl) pentaerythrityl-diphosphite and distearyl-pentaerythrityl diphosphite.

4. A composition according to any one of the preceding claims which contains one or more additional antioxidants.

5. A composition according to Claim 4 in which the additional antioxidants are selected from sterically hindered phenolic antioxidants, aminoaryl antioxidants or sulphur containing antioxidants.

6. A composition according to Claim 5 in which the phenolic antioxidants are selected from octadecyl-3-(3',5'-ditert.-

butyl-4'-hydroxyphenyl)-propionate, pentaerythrityl-tetrakis-3-(3',5'-ditert.butyl-4'-hydroxyphenyl)-propionate, 1,3,5-tris-(3',5'-di-t-butyl-4'-hydroxy-phenyl)-isocyanurate, 1,1,3,tris-(5'-tert.butyl-4'-hydroxy-2'-methylphenyl)-butane, 1,3,5-tris-(3',5'-ditert.butyl-4'-hydroxybenzyl)-mesitylene and ethylene glycol-bis-(3,3-bis-(3'-tert.butyl-4'-hydroxyphenyl)-butyrate).

7. A composition according to Claim 5 in which the aminoaryl antioxidants are selected from N,N'-dinaphthyl-p-phenylene diamine and N,N'-hexamethylene bis-3-(3,5-ditert.butyl-4-hydroxy-phenyl)-propionamide.

8. A composition according to Claim 5 in which the sulphur containing antioxidants are selected from di-tridecyl-3,3-thiodipropionate, di-lauryl-3,3'-thiodipropionate, distearyl-3,3'-thiodipropionate, methane tetrakis-(methylene -3-hexyl thiopropionate) and dioctadecyl-disulphide .

9. A composition according to any one of the preceding claims containing as a further additive alpha tocopherol (Vitamin E).

10. A composition according to any one of the preceding claims in which the amount of component a) present is from 70 to 40% by weight and the amount of component b) present is from 30 to 60%, by weight of the composition.

11. A composition according to Claim 10 in which the amount of component a) present is 40-60% by weight and the amount of component b is 60-40% by weight of the composition.

12. A composition according to Claim 4 or any one of Claims 5 to 11 when appendant to Claim 4 in which the additional antioxidant (or Vitamin E) is present in an amount of 50 to 200%, by weight of components a) and b) of the composition.

13. A polymeric composition comprising a polymeric material and a stabilising amount of a stabilising composition according to any one of the preceding claims.

14. A polymeric composition according to Claim 13 in which the amounts of components a) and b) present are from 0.01 to 1 % by weight based on the polymeric material.

15. A stabilising composition according to Claim 1 substantially as herein described with reference to the any one of Examples 1 to 4.

16. A polymeric composition according to Claim 4 substantially as herein described with reference to the any one of Examples 1 to 4.

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